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PATENT SPECIFICATION (11) 1 590 728

(21) Application No 43950/77 (22) Filed 21 Oct 1977

(44) Complete Specification Published 10 Jun 1981

(51) INT. CL.[3] B22F 3/00

(52) Index At Acceptance C7D 8A1 8D 8Z12 8Z5 A1

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(19)

(54) METHOD FOR PREPARING A FIBER REINFORCED METAL COMPOSITE

(71) We, SILAG, INC., a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of 1251 Avenue of the Americas of New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for preparing a fiber-reinforced metal composite, being more especially concerned with a metal composite reinforced with microscopic fibers.

Increasing demands for very strong, lightweight metals have fostered the development of a number of techniques for producing fiber reinforced metal composites. The effective incorporation of high strength single crystal fibers or whiskers in a metal matrix results in a combination of the mechanical properties of the metal with those of the high strength fibers. For example, normal metallurgical processes can produce a metal alloy of enhanced strength, but the stiffness of the metals will remain the same. However, if whiskers of silicon carbide, which has a stiffness of approximately 75 million psi, are combined with aluminum, which has a stiffness of approximately 10 million psi, a metal composite having a stiffness much greater than that of aluminum will result. Such a composite consisting of 80 percent by volume of aluminum and 20 percent by volume of silicon carbide whiskers would have a stiffness substantially equal to that of steel with no appreciable increase in weight. This would provide aluminum having the stiffness of steel but the corrosion resistance and light weight of aluminum.

Many of the difficulties encountered in the production of a fiber reinforced metal composite and novel methods for resolving these difficulties are disclosed in our issued United States Patent Numbers 3,441,392; 3,498,890; 3,668,748; 3,828,417 and 3,833,697. While the processes disclosed in these patents are highly advantageous over processes disclosed in the art prior thereto, these processes all relate to the production of metal composites using whiskers of relatively large size. The whiskers employed in these processes were of a diameter in the tens of micron range; normally up to 30 microns, and had lengths of up to one half inch. Subsequently, ceramic fiber technology has advanced to a point where microscopic whiskers having diameters extending from the submicron range to an upper limit of under ten microns are readily available. VM0032 graphite whiskers marketed by Union Carbide Company are available in diameters ranging from 1 to 9 microns, while silicon carbide whiskers marketed by Exxon Enterprises of Salt Lake City, Utah, have diameters in the submicron range of from 500 to 1000 angstroms.

Microscopic whiskers used as reinforcement for a metal will provide a superior metal composite product. A uniform dispersion of these whiskers throughout a composite will provide a large number of strength imparting fibers for any given area. For example, in uncombined form, about 250 million of the Exxon silicon carbide fibers will occupy only about one cubic inch. The length of these fibers is less than the diameter of the fibers conventionally used in known metal composite forming processes.

Heretofore, microscopic ceramic whiskers having diameters extending from the submicron to below 10 micron range have been found to be unsuitable for use in metal matrix composites. For example, with silicon carbide fibers having diameters of 500 - 1000 angstroms, it is difficult to bond epoxy or molten plastic around the fibers without creating holes or voids, and with metal powder, this difficulty is multiplied. It is necessary to uniformly disperse the fibers throughout the metal powder and to then maintain this uniform dispersion as the powder-fiber mixture is placed in a die cavity for molding.

It is an object of the present invention to provide a novel and improved process for

making a fiber-reinforced metal matrix composite, especially such a composite reinforced with microscopic fibers.

According to the present invention there is provided a process for preparing a fiber-reinforced metal composite, comprising the steps of

(a) mixing a metal powder with ceramic fibers;

(b) extruding the mixture at least three times to obtain a substantially uniform dispersion of fibers throughout the metal powder-fiber mixture;

(c) cold pressing the extruded mixture at a first densification pressure;

(d) heating the cold pressed mixture to a temperature sufficient to permit subsequent further densification thereof;

(e) further densifying the heated mixture by hot pressing at a second densification pressure; and

(f) cooling the resultant composite.

Very preferably the fibers constitute microscopic fibers having a diameter less than 10 microns. Silicon carbide fibers of from 500 to 1000 Å diameter are especially suitable.

Normally the pressure employed for step (c) is from 500 to 4000 psi, and very preferably from 1000 to 1500 psi.

Broadly, step (a) of the process of the present invention involves the preparation of the metal powder and fiber mixture. The metal should constitute fine metal powder of preferably minus 200 mesh, most preferably minus 325 mesh. Suitable metal powders are specified in our U.S. Patent Numbers 3,441,392, 3,668,697 and 3,833,697. Suitable pure aluminum powder and aluminum powder composition in the minus 325 mesh range, designated 6061, 2024, 7075, 5052 and 1100, may be obtained from Reynolds Aluminum Company, Richmond, Virginia.

The fiber and metal powder are first weighed so that, preferably, the fiber constitutes 10 to 30 percent of the total volume of the mixture. The preferred fiber volume is approximately 20 percent, as this has been found the easiest to incorporate into the metal matrix. It is highly preferred that the fiber is of a diameter of less than 10 microns and might constitute graphite or silicon carbide fibers. These fibers are microscopic and in a random oriented form. Individual fibers have no apparent length unless viewed under a microscope.

After the fiber and metal powder portions are determined by weighing, they are placed in a large container and agitated. In a preferred embodiment of the invention this agitation will occur in a molten, distilled, camphene vehicle, suitably for between 5 and 15 minutes. The volume of the molten, distilled camphene employed must at least equal and preferably exceeds the total volume of the fiber-metal powder mixture. Alternatively the fibers and metal powder are first mixed, followed by mixing with the vehicle.

A vehicle such as molten, distilled, camphene has been found to be useful once the microscopic fibers have been dispersed and oriented in the metal matrix to maintain the fiber dispersion and orientation. The vehicle employed for this purpose must have a low melting point, must not react with the metal matrix employed, must evaporate leaving substantially no residue and must be able to be extruded at room temperature.

Crude camphene sold by either the Eastman Kodak Company or the Glidden Durkee Company is readily available, but crude camphene has been found to attack aluminum and other metal powders. However, a simple vacuum distillation of crude camphene renders it suitable for use in the process of this invention. It has been found that distilled camphene obtained by subjecting crude camphene to only one vacuum distillation cycle operates effectively as a suitable vehicle, although purer distilled camphene obtained from a plurality of distillation cycles is even more preferable.

Distilled camphene melts at approximately 52°C. and molten distilled camphene is inserted into the mixing container with the measured portions of metal powder and microscopic fiber. After agitation and mixing in the container, suitably for from 5 to 15 minutes, the resultant mixture is cooled under refrigeration until all of the camphene solidifies.

The refrigerated mixture of metal powder and fibers in the camphene vehicle is extremely poor at best. The fibers are much lighter than the metal matrix, and generally the fiber size and shape and metal powder particle sizes vary markedly. If a sound, composite metal billet is to be obtained from this mixture, the fiber must be evenly distributed throughout the metal matrix.

To achieve good fiber-metal powder distribution, the refrigerated mixture is extruded at room temperature after the camphene vehicle has solidified. The refrigerated block containing the mixture is extruded through a conventional extrusion die, and this process of extrusion is repeated at least three times. The plurality of extrusions of the mixed material results in an excellent distribution of the microscopic fibers throughout the metal powder matrix. Although a minimum of three extrusions is required, additional extrusions can be accomplished until the best distribution is obtained. After three extrusions have been accomplished, the fiber distribution should be checked with a microscope and should be rechecked after each additional extrusion step.

Once the extrusion process has been completed, the camphene-fiber-powder mixture is placed in a vacuum chamber and the chamber is evacuated to cause vacuum evaporation of the camphene. The evaporated camphene may be retained and reused, and when all camphene is evaporated from the mixture, the now dry

mixture is ready for consolidation into billets.

The apparatus for billet preparation is quite conventional and includes a cylindrical steel or graphite die, a punch or plunger, a heater, a thermocouple for temperature measurement and a (hydraulic) press. Such an apparatus suitable for use in accomplishing the present method is shown in our U.S. Patent Number 3,441,392.

The dry mixture is gently poured into the die cavity, and the metal powder, apparently only loosely attached to the fibers, does not segregate. It is likely that the residual thin oil film left from the camphene constituents may be responsible for this beneficial behavior. If the mixture were to segregate, the distribution would suffer and billet quality would be poor.

After the die cavity has been filled with the mixture, a punch is placed in the cavity and a pressure of at least 500 psi and preferably of from 1000 to 1500 psi is applied to the mixture by means of the punch. Once again, because of the film left by the mixing vehicle over the powder and the fiber, the damage to the fiber due to this load is minimal, for apparently, the film acts as a lubricant. It is important to note that, unlike the process described in Patent Number 3,441,392, the process of this invention involves the application of pressure to the mixture in the die cavity while the mixture is at room temperature.

In another embodiment of the invention, step (a) is conducted by mixing the ceramic fibers with magnesium powder, heating in an inert atmosphere to evaporate the magnesium and form a coating thereof on the fibers, mixing the magnesium coated fibers with aluminum powder to alloy with the magnesium, and subsequently mixing in additional aluminum powder, suitably to give said 10 to 30% of percent total. The dry mix is then poured and pressed as described in the previous two paragraphs.

In all cases the whole die assembly is now quickly heated to a temperature above the melting point of the metal powder with the punch in place but with little or no additional pressure on the punch. A calculated second pressure is now applied, since the volume of the die and the amount of mixture in the die are known, the volume that the mixture would occupy if 100% densified is calculated. For example, 2.7 grams of aluminum will occupy a volume of 1 cubic centimeter if free of voids. Similarly, 2,7 grams of aluminum with 3.17 grams of silicon carbide fibers will occupy 2 cubic centimeters if fee of voids. By using the Law of Mixtures to calculate the volume that the mixture within the die would occupy if free of voids, the necessary punch movement into the die to leave only this void free volume can be calculated. Thus the necessary punch movement which is to occur after the die cavity has been heated to cause the mixture to pass into a semi-molten state is precalculated (the semi-molten mixture comprises solid fibers in a substantially molten metal phase). Whatever pressure that is needed to move the punch downward to that distance is utilized and it generally exceeds 2000 psi. All the air is expelled from the mixture and the molten metal encapsulates the fibers simultaneously. The ram travel is deliberately approximately 5 percent more than that calculated to assure complete densification, and the excess molten metal escapes from the die via the annular space between the die and the punch.

The 5% excess travel of the punch within the die cavity may be easily obtained by making the volume calculations at room temperature. Since the mixture within the die cavity is heated when pressure is reapplied thereto, thermal expansion of the mixture provides the slight excess needed to assure that the pressed billet is substantially free of voids. The pressure is maintained and the die and billet are allowed to cool. The cool billet is then ejected from the die and is ready to use.

The temperatures necessary to bring various metal-fiber mixtures to a semi-molten state for the final pressure step are completely discussed in our U.S. Patents Numbers 3,441,392 and 3,833,697, and the apparatus and temperatures discussed in those patents are used to perform the method of the present invention. As previously stressed, the present method of forming the finished billet differs from that disclosed in the aforementioned patents in that pressure is first applied to the mixture in the die at room temperature. The die is then retained against the initially compressed mixture while the temperature of the die cavity is raised to cause the mixture to pass into the semi-molten state discussed in the aforementioned patents. Then the punch is driven to the predetermined point in the die to achieve the desired billet densification.

When microscopic fibers have been evenly dispersed throughout a metal powder-fiber mixture, they may be subjected to pressure at room temperature without damaging the fibers. This cold pressure step is extremely advantageous, as it removes most of the voids in the mixture before heating and consequently eliminates any substantial relative movement between the metal powder particles and the fibers which might occur after heating to upset the even dispersal of fibers throughout the semi-molten mixture. The application of significant pressure to the mixture before heating compresses the mixture and makes it easier to maintain an even temperature throughout the mixture during the subsequent pressure step as the mass of the mixture to be heated is now much smaller.

The process of the present invention has been employed effectively with both microscopic graphite and silicon carbide fibers in the manner indicated by the following examples.

Example 1 employs a molten, distilled, camphene vehicle. Example 2 does not employ any mixing aid. Example 3 illustrates magnesium powder as a mixing aid.

EXAMPLE 1

Graphite fibers (VM 0032, Union Carbide Company) having diameters within the range of 1 to 9 microns were placed in a mixer with aluminum powder (minus 325 mesh) and molten distilled camphene. The graphite fibers constituted 20% by volume of the total fiber-metal powder mixture. The mixture was agitated for between 5 to 15 minutes and then refrigerated until the camphene solidified. The solidified mixture was then extruded four times, and subsequently wrapped in a paper towel and placed in a vacuum chamber. The camphene was then vacuum evaporated, and the dry mixture was then carefully placed in a die cavity. A punch was then inserted into the cavity and the mixture initially compressed at room temperature under at least 500 psi. After initial compression with no added pressure on the punch, the die was heated to above the melting point of the aluminum powder, and the punch was then moved inwardly to decrease the die cavity to at least the cavity size occupied by the mixture at a theoretical 100% density. The cavity was then cooled with the punch in place and the finished billet ejected.

EXAMPLE 2

Silicon carbide fibers (Exxon Enterprises) having diameters within the range of from 500-1000 angstroms were placed in a container with aluminum powder (minus 325 mesh) and kneaded together to disintegrate any fiber lumps and to adhere the powder to the fiber. The silicon carbide fibers constituted 20% by volume of the fiber-metal powder mixture, and when kneaded, the extremely fine fibers formed a mixture with the powder having a "dough-like" consistency, thereby eliminating the need for a mixing vehicle such as camphene. This "doughy" mixture was then extruded three times at room temperature and placed in die cavity. A punch was inserted to compress the mixture under at least 500 psi at room temperature, and then, with no added pressure, the die was heated to above the melting point of the aluminum powder. The punch was then moved inwardly to decrease the die cavity in the manner previously described to obtain maximum density, the cavity was cooled and the finished billet ejected.

It has been found that microscopic silicon carbide fibers may be subjected to a pressure of up to 4000 psi during the cold pressure step which is extremely advantageous, for these fibers remain evenly distributed in the metal powder during a cold pressure step. Conversely, if the mixture is first heated to a semi-molten state, the movement of the fibers in the semi-molten metal is much greater.

EXAMPLE 3

A vehicle other than camphene may be employed to cause the metal to adhere to the microscopic fibers to form a billet substantially free of voids. Magnesium powder, which is generally highly flammable, may be alloyed with aluminum to provide such a vehicle.

Silicon carbide fibers (Exxon Enterprises) having diameters within the range of from 500-1000 angstroms were placed in an iron crucible with magnesium powder (minus 250 mesh) and the mixture was heated in an inert atmosphere to a temperature below the melting point of magnesium but high enough to enhance the evaporation of the magnesium (i.e. 600 degrees C.). The mixture was stirred while heating until the fibers turned brown by the adherence thereto of the evaporating magnesium. Then aluminum powder (minus 350 mesh) was added to the hot mixture and the mixture was stirred until the fibers turned grey. A eutectic forms where the aluminum powder meets the magnesium and the aluminum melts, spreads and adheres. Because the magnesium alloys with the aluminum, the coated fibers are not flammable. The coated fibers are cooled and mixed with a sufficient amount of added aluminum powder so that the fibers constitute substantially 20% by volume of the mixture and all the post-mixing steps of Example 2 were then carried out to form a billet.

In all cases, the cold pressing step employed in the method of the present invention makes it unnecessary to control the subsequent heating of the mixture only to a degree necessary to maintain the metal or alloy in a state between the solidus and liquids thereof. Since the cold pressure step of the present invention substantially positions the fibers in their final position in the mixture, the mixture may subsequently be heated to a point far above the melting point of the metal or alloy powder so that the metal or alloy powder is completely molten during the final hot pressing step.

WHAT WE CLAIM IS:—

1. A process for preparing a fiber-reinforced metal composite, comprising the steps of (a) mixing a metal powder with ceramic fibers;

(b) extruding the mixture at least three times to obtain a substantially uniform dispersion of fibers throughout the metal powder-fiber mixture;

(c) cold pressing the extruded mixture at a first densification pressure;

(d) heating the cold pressed mixture to a temperature sufficient to permit subsequent further densification thereof;

(e) further densifying the heated mixture by hot pressing at a second densification pressure; and

(f) cooling the resultant composite.

2. A process according to Claim 1, wherein said fibers constitute microscopic fibers having a diameter of less than 10 microns.

3. A process according to Claim 1 or Claim 2, wherein the metal powder is of minus 200 mesh particle size.

4. A process according to any preceding claim, wherein step (a) comprises dry mixing the metal powder and ceramic fibers in amounts such that the fibers constitute from 10 to 30 vol. % of the total volume of the mixture.

5. A process according to any preceding claim, wherein the metal powder is aluminum powder.

6. A process according to any preceding claim, wherein the mixing step (a) is conducted in the presence of, or is followed by a further mixing with, at least an equal volume of molten, distilled camphene, which camphene is subsequently evaporated from the resultant mixture after the extrusion step (b) and before the cold pressing step (c).

7. A process according to Claim 5, wherein the metal powder-fiber mixing step (a), is conducted by mixing said ceramic fibers with magnesium powder, heating the mixture in an inert atmosphere to evaporate the magnesium and form a coating thereof on said ceramic fibers, mixing the magnesium coated fibers with aluminum powder to alloy the aluminum powder with the magnesium, and subsequently adding and mixing in additional aluminum powder.

8. A process according to any preceding claim, wherein the ceramic fibers are graphite fibers or silicon carbide fibers.

9. A process according to Claim 8, wherein the silicon carbide fibers are of 500 to 1000 Å in diameter.

10. A process according to any preceding claim, wherein step (c) is conducted at 500 to 4000 psi.

11. A process according to Claim 10, wherein step (c) is conducted at 1000 to 1500 psi.

12. A process according to any preceding claim, wherein the heating in step (d) is sufficient to raise the temperature of the metal powder above its melting point.

13. A process according to any preceding claim and substantially as herein described.

14. A process as claimed in Claim 1 and substantially as herein described with reference to any one of Examples 1 to 3.

15. A fiber-reinforced metal composite whenever prepared by a process according to any preceding claim.

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Printed for Her Majesty's Stationery Office by MULTIPLEX techniques ltd., St. Mary Cray, Kent. 1981. Published at the Patent Office, 25 Southampton Buildings, London WC2 1AY, from which copies may be obtained.